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(71) Applicant (for all designated States except US): **OMG KOKKOLA CHEMICALS OY [FI/FI]; P.O. Box 286, FIN-67101 Kokkola (FI).**

(72) Inventor; and

(75) Inventor/Applicant (for US only): **MARTIKAINEN, Mika [FI/FI]; Hakalahdenkatu 83 B 22, FIN-67100 Kokkola (FI).**

(74) Agent: **BERGGREN OY AB; P.O. Box 16, FIN-00101 Helsinki (FI).**

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(54) Title: **PROCESS FOR MAKING HIGH DENSITY AND LARGE PARTICLE SIZE COBALT HYDROXIDE OR COBALT MIXED HYDROXIDES AND A PRODUCT MADE BY THIS PROCESS**

(57) Abstract: The invention relates to a method for preparing a cobaltous hydroxide with a high density and a large particle size or an alloy hydroxide of cobalt and some other metal, in which a complexing agent and hydroxide ion is added to an aqueous cobalt brine or an aqueous brine of cobalt and some other metal under alkaline conditions in order to form a metal hydroxide. In this method, the complexing agent is selected so as to form an ammonium complex with the metal ion. The molar ratio of complexing agent to metal is about 0.5-3, and the pH is regulated in the range 10-13.

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Process for making high density and large particle size cobalt hydroxide or cobalt mixed hydroxides and a product made by this process

5 The invention relates to a method for preparing cobaltous hydroxide with a high density and a large particle size or an alloy hydroxide of cobalt and some other metal. The invention also relates to the product produced with this method.

10 Cobaltous hydroxide is used in many applications, for instance as an additive in chargeable NiMH and NiCd accumulators in the electronics industry. In addition, it is suitable for use as a precursor in the preparation of oxide products, such as LiCoO_2 and LiCoMO_2 (M stands for metal). Cobaltous hydroxide is also used as a catalyst or a precursor in catalyst production. A hydroxide product comprising any other metal in addition to cobalt, such as nickel, manganese, magnesium or aluminium, is also suitable for use for the purposes mentioned above.

15 There are many known methods for preparing cobaltous hydroxide in the field. The method of US patent 5,057,299 prepares cobaltous hydroxide by combining a cobaltous ion with a complexing agent, thus producing a water-soluble cobalt complex. Hydroxide ion is added to this, and the mixture is heated and kept in hydrothermal conditions until the cobaltous hydroxide precipitates. With the method of this US patent, the particle size increases at higher temperatures. Nonetheless, the
20 method of the patent allows the particle size to be controlled only in the range from approx. 0.05 to 0.5 μm by means of the temperature.

In applications of the accumulator industry, NiCd and NiMH accumulators are required to have good capacity. The capacity can be raised by using cobaltous hydroxide with maximum density as an additive in accumulators. In addition to this,
25 it is important that the cobaltous hydroxide used in the production of oxide products has a small specific surface and a high density. The purpose of the present invention is to provide a method for preparing cobaltous hydroxide particles with a large particle size or alloy hydroxide particles of cobalt and some other metal with a method that is easy to control. The purpose is to achieve cobaltous hydroxide
30 particles or alloy hydroxide particles of cobalt and some other metal with a particle size above 1 μm , preferably above 3 μm . This has been achieved according to the invention in the manner described in the accompanying claims.

Besides cobaltous hydroxide, the method in accordance with the invention can be used to prepare alloy hydroxides of cobalt and one or more other metals. The other

metals used may comprise for instance nickel, manganese, magnesium or aluminium, or alloys of these, depending on the purpose of use.

The starting material used in the method of the invention is an aqueous brine of cobalt or cobalt and alloy metals in the form of sulphate, nitrate or chloride. The
5 concentration of the solution may vary in the range from 10 to 120 g/l calculated on the total metal content.

A complexing agent that forms an ammonium complex with the metal ion is added to this metal brine. The complexing agent may be ammonium sulphate, aqueous ammonia or any other ammonium ion source. In principle, the complexing agent
10 may also be some other substance forming a complex with a metal, such as for instance EDTA. In the present invention, ammonium ion has nevertheless proved a good complexing agent owing to its economic price and good complexing characteristics. The molar ratio of the ammonium complexing agent to the metal introduced in the reactor is preferably about 0.5-3, most preferably about 1.5-2.0.
15 The reaction is performed under alkaline conditions and NaOH is preferably used for pH regulation. The preferred pH is in the range 10-13, most preferably the pH is in the range 11.2-12.0. The reaction is carried out at a temperature of about 40-90 °C, preferably at a temperature of about 70 °C. The method in accordance with the invention yields cobaltous hydroxide with a density of about 0.5-2.2 g/cm³, a
20 particle size above approx. 1 µm, typically approx. 1-20 µm and a specific surface of approx. 0.5-20 m²/g.

The particles obtained with the method of the invention are plate-like cobaltous hydroxide particles in the shape of a hexagon. It was found in connection with the invention that chloride solutions yield thicker particles than sulphate-based
25 solutions, with the other reaction conditions unaltered. Thicker particles are considered more suitable for instance for the preparation of lithium cobalt oxide.

In the method of the invention, the particle size of cobaltous hydroxide can be controlled by means of the molar ratio of the ammonium ion to the cobalt ion and of the pH used. Figure 1 shows the particle size variation as a function of pH with
30 varied ratios NH₃ ion/Co. The figure shows that a pH increase reduces the particle size, and that the higher the ratio NH₃ ion/Co, the more notable the effect of the pH on the particle size.

The invention is illuminated below by means of examples. In examples 1-3 the method has been carried out as a comparison without complexing with ammonium

ions. Examples 4-6 illustrate the method of the invention, in which an ammonium complex with cobalt is formed. Example 7 exemplifies the method of the invention, in which nickel was used in addition to cobalt. The reaction temperature in the examples was 70 °C.

5 Comparative example 1

An aqueous solution of CoCl_2 (30 g/l Co) was introduced continually into a first reactor. The pH was maintained constant in the range 11.8-12.0 by adding sodium hydroxide solution. The overflow of the first reactor was conducted to the second reactor, where sodium hydroxide was added to the flow, resulting in pH 13.5. The overflow from the second reactor was filtered and washed with water. The washed Co(OH)_2 cake was dried.

The average particle size D50 of the dried Co(OH)_2 was 0.9 μm when determined with a Malvern Mastersizer particle size analyser (the determination was performed with laser diffraction on an aqueous Co(OH)_2 slurry). The density was 0.5 g/cm^3 (ASTM B527-93). The specific surface (BET ASTM D4567-86) was 30 m^2/g .

Comparative example 2

An aqueous solution of CoCl_2 (30 g/l Co) was introduced continually into the first reactor. The pH was maintained constant in the range 11.6-11.8 by adding sodium hydroxide solution. The overflow of the first reactor was conducted to the second reactor, where sodium hydroxide was added to the flow so as to obtain pH 13.5. The overflow from the second reactor was filtered and washed with water. The washed Co(OH)_2 cake was dried.

The average particle size D50 of the dried Co(OH)_2 was 1.1 μm when determined with a Malvern Mastersizer particle size analyser (the determination was performed with laser diffraction on an aqueous Co(OH)_2 slurry). The density was 0.7 g/cm^3 (ASTM B527-93). The specific surface (BET ASTM D4567-86) was 29 m^2/g .

Comparative example 3

An aqueous solution of CoCl_2 (30 g/l Co) was introduced continually into the first reactor. The pH was maintained constant in the range 11.2-11.4 by adding sodium hydroxide solution. The overflow of the first reactor was conducted to the second reactor, where sodium hydroxide was added to the flow so as to obtain pH 13.5.

The overflow from the second reactor was filtered and washed with water. The washed Co(OH)_2 cake was dried.

5 The average particle size D50 of the dried Co(OH)_2 was $1.9 \mu\text{m}$ when determined with a Malvern Mastersizer particle size analyser (the determination was performed with laser diffraction on an aqueous Co(OH)_2 slurry). The density was 0.6 g/cm^3 (ASTM B527-93). The specific surface (BET ASTM D4567-86) was $35 \text{ m}^2/\text{g}$.

Example 4

10 An aqueous solution of CoCl_2 (30 g/l Co) was introduced continually into the first reactor, which contained an aqueous solution of ammonia with the molar ratio 2 metal/ammonia. The pH was maintained constant in the range 11.8-12.0 by adding sodium hydroxide solution. The overflow of the first reactor was conducted to the second reactor, where sodium hydroxide was added to the flow so as to obtain pH 13.5. The overflow from the second reactor was filtered and washed with water. The washed Co(OH)_2 cake was dried.

15 The average particle size D50 of the dried Co(OH)_2 was $1.8 \mu\text{m}$ when determined with a Malvern Mastersizer particle size analyser (the determination was performed with laser diffraction on an aqueous Co(OH)_2 slurry). The density was 0.7 g/cm^3 (ASTM B527-93). The specific surface (BET ASTM D4567-86) was $5.8 \text{ m}^2/\text{g}$.

Example 5

20 An aqueous solution of CoCl_2 (30 g/l Co) was introduced continually into the first reactor, which contained an aqueous solution of ammonia with the molar ratio 2 metal/ammonium. The pH was maintained constant in the range 11.6-11.8 by adding sodium hydroxide solution. The overflow of the first reactor was conducted to the second reactor, where sodium hydroxide was added to the flow so as to obtain
25 pH 13.5. The overflow from the second reactor was filtered and washed with water. The washed Co(OH)_2 cake was dried.

The average particle size D50 of the dried Co(OH)_2 was $3.9 \mu\text{m}$ when determined with a Malvern Mastersizer particle size analyser (the determination was performed with laser diffraction on an aqueous Co(OH)_2 slurry). The density was 1.2 g/cm^3
30 (ASTM B527-93). The specific surface (BET ASTM D4567-86) was $2.6 \text{ m}^2/\text{g}$.

Example 6

An aqueous solution of CoCl_2 (30 g/l Co) was introduced continually into the first reactor, which contained an aqueous solution of ammonia with the molar ratio 2 metal/ammonium. The pH was maintained constant in the range 11.2-11.4 by adding sodium hydroxide solution. The overflow of the first reactor was conducted to the second reactor, where sodium hydroxide was added to the flow so as to obtain pH 13.5. The overflow from the second reactor was filtered and washed with water. The washed Co(OH)_2 cake was dried.

The average particle size D50 of the dried Co(OH)_2 was $7.4 \mu\text{m}$ when determined with a Malvern Mastersizer particle size analyser (the determination was performed with laser diffraction on an aqueous Co(OH)_2 slurry). The density was 1.7 g/cm^3 (ASTM B527-93). The specific surface (BET ASTM D4567-86) was $1.8 \text{ m}^2/\text{g}$.

Example 7

An alloy brine was prepared which contained CoCl_2 and NiCl_2 solutions (30 g/l Co and 8g/l Ni). The solution was introduced continually into the first reactor, which contained an aqueous solution of ammonia with the molar ratio metal/ammonium being 2. The pH was maintained constant in the range 11.2-11.4 by adding sodium hydroxide solution. The overflow of the first reactor was conducted to the second reactor, where sodium hydroxide was added to the flow so as to obtain pH 13.5. The overflow from the second reactor was filtered and washed with water. The washed Co(OH)_2 cake was dried.

The chemical analysis indicated precipitation of alloy hydroxide. The average particle size D50 of the dried $\text{Co}_{0.8}\text{Ni}_{0.2}(\text{OH})_2$ was $6.9 \mu\text{m}$ when determined with a Malvern Mastersizer particle size analyser (the determination was performed with laser diffraction on an aqueous Co(OH)_2 slurry). The density was 1.6 g/cm^3 (ASTM B527-93). The specific surface (BET ASTM D4567-86) was $3.2 \text{ m}^2/\text{g}$.

To facilitate the comparison, the table below shows the physical properties of the products exemplified above. The table also shows the crystal size of the products, which was measured with an X-ray diffraction meter.

Table 1

Example	Precipitated pH	Complexing agent	Average particle size (μm)	Density (g/cm^3)	Specific surface (m^2/g)	XRD (001) (nm)	XRD (101) (nm)
Comparative example 1	11.8-12.0	None	0.9	0.5	30	23	27
Comparative example 2	11.6-11.8	None	1.1	0.7	29	26	30
Comparative example 3	11.2-11.4	None	1.9	0.6	35	27	32
Example 4	11.8-12.0	NH_3 ion	1.8	0.7	5.8	50	49
Example 5	11.6-11.8	NH_3 ion	3.9	1.2	2.6	56	56
Example 6	11.2-11.4	NH_3 ion	7.4	1.7	1.8	61	64
Example 7	11.2-11.4	NH_3 ion	6.9	1.6	3.2	59	57

5 The table shows that, with ammonium ion used as the complexing agent, the product had a larger particle size and higher density than without a complexing agent. As an exception from this, the product of example 4 had a particle size and a density approximately equal to those of the comparative examples. In fact, the specific surface and crystal size of this product also equalled the values of the products of examples 5-7.

10 A number of applications of the invention have been presented above. The invention is naturally not restricted to the examples above, its principle being variable within the scope of protection of the claims.

Claims

1. A method for preparing cobaltous hydroxide with a high density and a large particle size or an alloy hydroxide of cobalt and some other metal, in which a complexing agent and hydroxide ion is added under alkaline conditions to an aqueous cobalt brine or an aqueous brine of an alloy of cobalt and some other metal in order to form metal hydroxide, characterised in that the complexing agent is selected so as to form an ammonium complex with the metal ion, the molar ratio of complexing agent to metal being approx. 0.5-3 and the pH being regulated in the range 10-13.
2. A method as defined in claim 1, characterised in that the pH is regulated in the range 11.2-12.0.
3. A method as defined in claim 1, characterised in that the brine of cobalt or of the alloy of cobalt and some other metal is in the form of sulphate, nitrate or chloride.
4. A method as defined in claim 1, characterised in that the brine concentration is in the range from 10 to 120 g/l calculated on the total metal content.
5. A method as defined in claim 1, characterised in that the complexing agent is ammonium sulphate or aqueous ammonia
6. A method as defined in claim 1, characterised in that the molar ratio of complexing agent to metal is approx. 1.5-2.
7. A method as defined in claim 1, characterised in that NaOH is used for pH regulation.
8. A method as defined in claim 1, characterised in that the reaction is carried out at a temperature of about 40-90 °C.
9. A method as defined in claim 8, characterised in that the reaction is carried out at a temperature of about 70 °C.
10. A method as defined in claim 1, characterised in that the other metals used are nickel, manganese, magnesium or aluminium, or alloys of these.
11. Cobaltous hydroxide or alloy hydroxide formed of cobalt and some other metal, characterised in having a density of about 0.5-2.2 g/cm³, a particle size

above about 1 μm , typically about 1-20 μm , and a specific surface of about 0.5-20 m^2/g .

12. Cobaltous hydroxide or alloy hydroxide formed of cobalt and some other metal, characterised in that the other metal is nickel, manganese, magnesium or
5 aluminium, or an alloy of these.

13. The cobaltous hydroxide or alloy hydroxide of cobalt and some other metal as defined in claim 11 or 12, characterised in being prepared with a method of any of claims 1-10.

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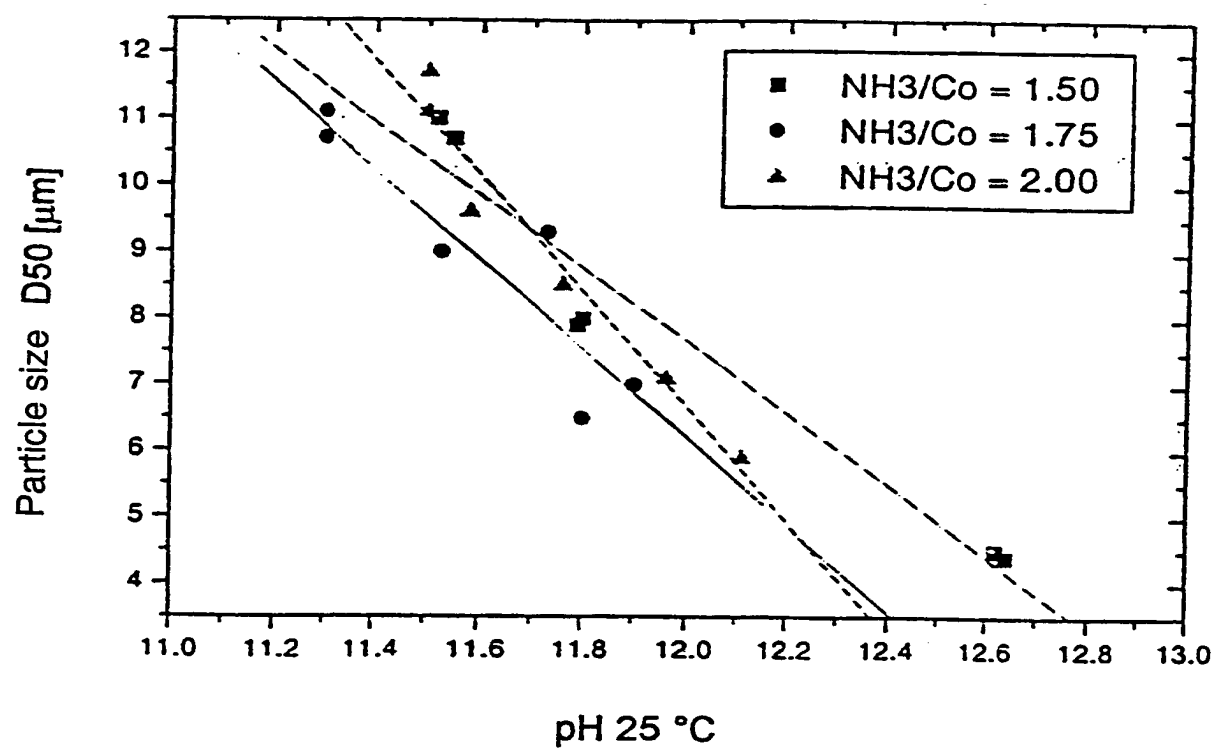


Figure 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 00/00581

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C01G 51/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5569444 A (PHILIPPE BLANCHARD ET AL), 29 October 1996 (29.10.96), column 3, line 47 - line 61, claim 1, abstract --	1-13
A	US 5057299 A (JEAN A. LOWN), 15 October 1991 (15.10.91), claim 1, abstract -- -----	1-13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Swedish Patent Office

Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Authorized officer

Moa Grönkvist/ELY

Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report			Publication date	Patent family member(s)		Publication date
US	5569444	A	29/10/96	AT	114873 T	15/12/94
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